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(54) CATIONIC ELECTRODEPOSITION COATING COMPOSITION, METHOD FOR FORMING FILM AND COATED PRODUCT HAVING FILM

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a new cationic electrodeposition coating composition using a resin composition having sulfonium groups and propargyl groups and carrying out film curing by photopolymerization after the coating, to provide a method for forming the film and to thereby realize low-temperature curing and short-time curing.

SOLUTION: This cationic electrodeposition coating composition is characterized as comprising the resin composition having the sulfonium groups and propargyl groups and a photopolymerization initiator.

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CLAIMS

[Claim(s)]

[Claim 1] A resin constituent with a sulfonium radical and a propargyl radical, and the cation electrodeposition paint constituent characterized by including a photopolymerization initiator.

[Claim 2] A photopolymerization initiator is a cation electrodeposition paint constituent according to claim 1 which is 0.2 – 8 % of the weight to the resin solid content weight in a cation electrodeposition paint constituent.

[Claim 3] The resin constituent with a sulfonium radical and a propargyl radical is a cation electrodeposition paint constituent according to claim 1 or 2 whose sum total content of a sulfonium radical and a propargyl radical 10–495mmol content of 5 – 400mmol and the propargyl radical is carried out per 100g of resin solid content in a cation electrodeposition paint constituent, and for a sulfonium radical, and is 500 or less mmols.

[Claim 4] The resin constituent with a sulfonium radical and a propargyl radical is a cation electrodeposition paint constituent according to claim 1, 2, or 3 whose sum total content of a sulfonium radical and a propargyl radical it consists of resin which makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, and has 700–5000 as number average molecular weight, 20–395mmol content of 5 – 250mmol and the propargyl radical is carried out per 100g of solid content of said resin constituent, and for a sulfonium radical, and is 400 or less mmols.

[Claim 5] The paint film formation approach which carries out electropainting of the cation electrodeposition paint constituent according to claim 1, 2, 3, or 4 to a coated object, and is characterized by including the process which irradiates ultraviolet rays at the coat obtained.

[Claim 6] Furthermore, the paint film formation approach including the process which heats the coat obtained according to claim 5.

[Claim 7] All or a part of time amount which performs UV irradiation is the paint film formation approach according to claim 6 which is what heats to coincidence.

[Claim 8] The coated object characterized by having the paint film obtained by the paint film formation approach according to claim 5, 6, or 7.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the coated object which has the paint film obtained in more detail by the paint film formation approach and it using the cation electrodepositon paint constituent in which hardening by ultraviolet rays is possible, and this about the coated object which has the paint film obtained by the paint film formation approach and it which uses a cation electrodepositon paint constituent and this.

[0002]

[Description of the Prior Art] Generally, the painting process of an automobile etc. consists of carrying out heat hardening of an intermediate coat and the paint film which top coat is subsequently painted and is obtained, after carrying out the under coat paint by the cation electrodepositon paint to the coated object to which chemical conversion was beforehand performed by phosphate etc.

[0003] Among these, cation electrodepositon performed as under coat paint is performed considering corrosion prevention, rust proofing, etc. as a key objective, and the cation electrodepositon paint containing a resin constituent with a sulfonium radical and a propargyl radical is indicated by JP 2000-36525A. The cation electrodepositon paint containing a resin constituent with this sulfonium radical and a propargyl radical is excellent in hardness and throwing power of electrolytic colouring.

[0004] On the other hand, conventionally, since the configuration is complicated, as for photo-curing, light is not usually used for the photocuring approach applied to the car body and components of an automobile in homogeneity.

[0005]

[Problem to be Solved by the Invention] The purpose of this invention offers the new cation electrodepositon paint constituent and the paint film formation approach of making photocopolymerization perform paint film hardening after cation electrodepositon using the resin constituent which has a sulfonium radical and a propargyl radical as paint film plasticity resin, and is for this to realize adhesion and short-time hardening.

[0006]

[Means for Solving the Problem] When this invention person includes a photopolymerization initiator in the cation electrodepositon paint constituent containing a resin constituent with a sulfonium radical and a propargyl radical [when performing the optical exposure of UV irradiation etc. on the electrodeposited coat obtained by cation electrodepositon] A header and this invention were completed for hardening of an electrodeposited coat progressing by the sulfonium radical contained in an electrodeposited coat generating a radical in response to an optical exposure, and this radical's acting on alone association generated with the electrodeposited coat, and making a polymerization perform.

[0007] That is, this inventions are a resin constituent with a sulfonium radical and a propargyl radical, and a cation electrodepositon paint constituent characterized by including a photopolymerization initiator. As for the above-mentioned photopolymerization initiator, It is desirable that it is 0.2 - 8 % of the weight to the resin solid content weight in the above-

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mentioned cation electrodepositon paint constituent. The resin constituent with the above-mentioned sulfonium radical and a propargyl radical carries out 10-45mmol content of 5 - 400mmol and the propargyl radical per 100g of resin solid content in the above-mentioned cation electrodepositon paint constituent, and for a sulfonium radical, and it is desirable that the sum total content of a sulfonium radical and a propargyl radical to 500 or less mmols. The resin constituent with the above-mentioned sulfonium radical and a propargyl radical consists of resin which makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin again, has 700-5000 as number average molecular weight, and carries out 20-35mmol content of 5 - 250mmol and the propargyl radical per 100g of solid content of the above-mentioned resin constituent, and for a sulfonium radical, and it is desirable that the sum total content of a sulfonium radical and a propargyl radical is 400 or less mmols.

[0008] This invention is the cation electrodepositon approach which carries out electrocoating of the above-mentioned cation electrodepositon paint constituent to a coated object, and is characterized by including the process which irradiates ultraviolet rays at the time obtained again. As for the above-mentioned cation electrocoating approach, it is desirable that it is a thing including the process which heats the coat obtained further, and, as for all or a part of time amount which performs the above-mentioned UV irradiation, it is more desirable that it is what heats so coincidence. This invention is a coated object characterized by having further the coat obtained by the above-mentioned cation electrocoating approach. However, this invention is explained to a detail.

[0009] The cation electrodepositon paint constituent of cation electrodepositon paint constituent, this invention contains a photopolymerization initiator. It is not limited especially as the above-mentioned photopolymerization initiator. For example, a benzoin, benzoin isopropyl ether, Benzoin, such as benzoin isobutyl ether; a benzophenone, Benzophenone, such as a 4 and 4'-cresol (dimethylamine) benzophenone (MIRAZU Aetona); Xanthene, Xanthene, such as a thioxanthone, 1,2-phenyl-2-hydroxy-acetophenone, An alpha and alpha-dichloro-1-phenylacetophenone, 1-hydroxy cyclohexylphenyl ketone, 2 and 2'-dihydroxy acetophenone, 2-hydroxy-2-methyl-1-phenyl-propane-1-OAc. Acetophenones, such as a 2-hydroxy-2-methyl-acetophenone, 2, and 2-dimethoxy-2-phenyl acetophenone (benzyl dimethyl ketone). In addition to this 4-dimethylaminophenyl benzene, 4, 4'-diazide stilbene-2, 2'-diazidin solid, 1,1-phenyl-1,1-2-propene diene-2-(2-ethoxyacetoxy) oxide, etc. can be mentioned. Especially, benzyl dimethyl ketone is desirable. One part or two parts or more can be used for these. The above-mentioned photopolymerization initiator can be prepared by the well-known approach, for example, a commercial item can also be used for it.

[0010] As for the above-mentioned photopolymerization initiator, it is desirable that it is 0.2 - 8 % of the weight to the resin solid content weight in the cation electrodepositon paint constituent of this invention. If photopolymerization may become inadequate when it is less than 0.2 % of the weight, and it exceeds 8 % of the weight, it is easy to produce unevenness in extent of hardening, and may be inferior to paint film physical properties. Preferably, it is 1 - 5 % of the weight.

[0011] The cation electrodepositon paint constituent of this invention contains a resin constituent with a sulfonium radical and a propargyl radical further. After painting an intermediate coat on the electrodepositon paint film which is not hardened [which the throwing power of electrolytic colouring in which the cation electrodepositon paint constituent of this invention was excellent in cation electrocoating is obtained by including such a resin constituent, and is described especially], both the sharp hardening paint film obtained can be used cuttable also for the double layer paint film formation approach heated to coincidence.

[0012] Although the resin which constitutes the above-mentioned resin constituents may have both sulfonium radical and propargyl radical in the mixed, the need does not exist, for example, may not necessarily have either the sulfonium radical or the propargyl radical further. In the case of this latter, it has these two sorts of all hardens functional groups as the whole resin constituent. That is, the above-mentioned resin constituent may consist of mixture of resin only with the resin and the propargyl radical which consist of resin with a sulfonium radical and a propargyl radical, or have only a sulfonium radical, or may consist of all these mixture. The resin constituent contained in the cation electrodepositon paint constituent of this invention has a

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sulfonium radical and a propargyl radical in above-mentioned semantic.

[0013] The above-mentioned sulfonium radical is a hydration functional group of the above-mentioned resin constituent. On an electrode, an ionicity radical can disappear in response to an electrolytic reduction reaction, and a sulfonium radical can be irreversibly nonconductORIZED, if the electrical potential difference or current more than fixed can be given in an electrocoating process. It is thought that the cation electrodepositon paint constituent of this invention can demonstrate advanced throwing power of electrolytic colouring by this.

[0014] In the electrocoating process in which the cation electrodepositon paint constituent of this invention is used electrode reaction is triggered, and when a sulfonium radical holds the produced hydroxide ion, an electrolysis generating base is considered to generate in an electrodeposited coat. This electrolysis generating base can change into reactant, high alkaline association by heating, the resultant low primary alkyl radical by heating which exists in an electrodeposited coat.

[0015] Especially as resin used as the frame of the resin constituent contained in the cation electrodepositon paint constituent of this invention, although not limited, an epoxy resin is used cutably. Poly glycidyl ether of the three association polybutadienes; novolak phenol mold Pori epoxy resin; novolak cresol mold Pori epoxy resin poly glycidyl acrylates; aliphatic acrylate polyol which specifically [as an epoxy resin, what has at least two or more epoxy group is suitable used into 1 molecules, and] carried out chain extension of an EPICLUS epoxy resin and this by di, dicarboxylic acid, diamine, etc., or polyether polyol; the Pori epoxy resin, such as poly glycidyl ether of a polyisobutylene carboxylic acid, can be mentioned. Since the formation of a polyfunctional radical for raising hardenability is [among these] easy, a novolak phenol mold Pori epoxy resin; a novolak cresol mold Pori epoxy resin, and poly glycidyl acrylates are desirable. In addition, some above-mentioned epoxy resins may be mono-epoxy resins.

[0016] The resin constituent contained in the cation electrodepositon paint constituent of this invention consists of resin which makes the above-mentioned epoxy resin frame, and number average molecular weight is 500-2000. The coating efficiency of cation electrocoating worsens that number average molecular weight is less than 500, and if 2000 is exceeded, a good coat cannot be formed on a coated object front face. When more desirable molecular weight can be set up according to a resin frame, for example, it makes a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin into a frame, as for the above-mentioned number average molecular weight, it is more desirable that it is 700-5000.

[0017] The contents of the sulfonium radical in the resin constituent in the cation electrodepositon paint constituent of this invention are per [5] 100g of resin solid content in the above-mentioned cation electrodepositon paint constituent - 400mmol after fulfilling the conditions of the content of the sulfonium radical mentioned later and a propargyl radical. Sufficient throwing power of electrolytic colouring, hardenability can be demonstrated as they are 5mmol(s) / less than 100g, and hydration and bath stability worsen. If it exceeds 400mmol(s) / 100g, a deposit of this coat on the front face of a coated object will worsen. When consisting of resin with which a more desirable content can be set up according to the resin frame used, for example, the above-mentioned resin constituent makes a frame a novolak phenol mold epoxy resin, as for the content of the above-mentioned sulfonium radical. It is more desirable that they are per [5] 100g of resin solid content in the cation electrodepositon paint constituent of this invention - 250mmol, and its 10 - 150mmol is still more desirable.

[0018] In the above-mentioned cation electrodepositon paint, although the reason of the propargyl radical in the resin constituent in the cation electrodepositon paint constituent of this invention is unknown, is not only acts as a hardening functional group, but it can raise further the throwing power of electrolytic colouring of the above-mentioned cation electrodepositon paint constituent by reacting with a sulfonium radical.

[0019] The contents of the propargyl radical in the resin constituent in the cation electrodepositon paint constituent of this invention are per [10] 100g of resin solid content in the above-mentioned cation electrodepositon paint constituent - 45mmol, after fulfilling the conditions of the content of the sulfonium radical mentioned later and a propargyl radical. When

sufficient throwing power of electrolytic colouring or hardenability cannot be demonstrated as they are 10mmol(s) / less than 100g, but it exceeds 45mmol / 100g, there is a possibility of having a bad influence on the hydration stability at the time of using it as a cation electrodepositon paint. When consisting of resin with which a more desirable content can be set up according to the resin frame used, for example, the above-mentioned resin constituent makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, as for the content of the above-mentioned propargyl radical, it is more desirable that they are per [20] 100g of resin solid content in the cation electrodepositon paint constituent of this invention - 250mmol.

[0020] Moreover, the sum total content of the sulfonium radical in the resin constituent contained in the cation electrodepositon paint constituent of this invention and a propargyl radical is 500 or less mmols per 100g resin solid content in the above-mentioned cation electrodepositon paint constituent - 500mmol(s) are exceeded, resin may not be obtained in fact or the largest organics performance may not be obtained. The sum total content of the sulfonium radical in the above-mentioned resin constituent and a propargyl radical can set up a more desirable content according to the resin frame used. For example, in the case of a novolak phenol mold epoxy resin and a novolak cresol mold epoxy resin, it is more desirable that they are 400 or less mmols.

[0021] A part of propargyl radical in the resin constituent contained in the cation electrodepositon paint constituent of this invention may be neutralized. An acetylidyne is the metal acetylidyne of salt resemblance. As for the content of the propargyl radical in the above-mentioned resin constituent acetylidyne-ized, it is desirable that they are per [0.1] 100g of resin constituent solid content - 40mmol. Acetylidyne is difficult, if the effectiveness according that they are less than 0.1 mmol to acetylidyne-izing not demonstrated enough but exceeds 40mmol. This content can set up the more desirable range according to the metal to be used.

[0022] Especially it is the metal which demonstrates a catalyst as a metal contained in the propargyl radical acetylidyne-ized [above]. It will not be limited, for example, transition metals, such as copper, silver, and barium, can be mentioned. If environmental compatibility is taken into consideration, copper and silver will be desirable and acquisition easiness to copper will be [among these] more desirable. When using copper, as for the content of the propargyl radical in the above-mentioned resin constituent acetylidyne-ized, it is more desirable that they are per [0.1] 100g of resin solid content in the cation electrodepositon paint constituent of this invention - 200mmol.

[0023] By acetylidyne-izing a part of propargyl radical in the resin constituent contained in the cation electrodepositon paint constituent of this invention, a curing catalyst can be introduced into resin. Since it can acetylidyne easily and can introduce even if it generally is not necessary to use the organic transition metal complex which dissolves or is hard to distribute for an organic solvent or water and is transition metals if it does in this way, even if it is a poorly soluble transition metals compound, it is freely usable as a coating constituent. Moreover, it is avoidable like [in the case of using a transition metals organic-salt salt] that an organic-salt exists during an electrodepositon bath as an anion. Further, a metal ion is not removed by ultrafiltration and the design of control of bath or a cation electrodepositon paint becomes easy.

[0024] The resin constituent contained in the cation electrodepositon paint constituent of this invention may be made to contain a carbon-carbon double bond by request. Since reactivity is high, the above-mentioned carbon-carbon double bond can raise hardenability further.

[0025] The content of the above-mentioned carbon-carbon double bond has per [10] 100g of resin solid content in the cation electrodepositon paint constituent of this invention - desirable 45mmol, after fulfilling the conditions of the content of the propargyl radical mentioned later and a carbon-carbon double bond. When sufficient hardenability cannot be demonstrated by addition as they are 10mmol(s) / less than 100g, but it exceeds 45mmol / 100g, there is a possibility of having a bad influence on the hydration stability at the time of using it as a cation electrodepositon paint. When consisting of resin with which a more desirable content can be set up according to the resin frame used, for example, the above-mentioned resin constituent makes

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a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, as for the content of the above-mentioned carbon-carbon double bond, it is more desirable that it is 20–35mmol.

[0022] When the resin constituent contained in the cation electrodeposition paint constituent of this invention contains the above-mentioned carbon-carbon double bond, as for the sum total content of the above-mentioned propargyl radical and a carbon-carbon double bond, it is desirable that it is within the limits of per 100g of resin solid content in the cation electrodeposition paint constituent of this invention 45mmol. If there is a possibility that hardenability may become less than 80 mmol inadequate and 45mmol is exceeded, the content of a sulfonium radical will decrease, and there is a possibility that throwing power of electrolyte colouring may become inadequate. When the resin constituent which can set up a more desirable content according to the resin frame used, for example, is contained in the above-mentioned cation electrodeposition paint constituent consists of resin which makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin, as for the sum total content of the above-mentioned propargyl radical and a carbon-carbon double bond, it is more desirable that it is 100–250mmol.

[0023] When the resin constituent contained in the cation electrodeposition paint constituent of this invention contains the above-mentioned carbon-carbon double bond, as for the sum total content of an above-mentioned sulfonium radical, propargyl radical, and carbon-carbon double bond, it is desirable that they are 500 or less mmol per 100g of resin solid content in the above-mentioned cation electrodeposition paint constituent. If 500mmol(s) are exceeded, resin may not be obtained in fact or the target engine performance may not be obtained. When consisting of resin with which a more desirable content can be set up, for example, the above-mentioned resin constituent makes a frame a novolak phenol mold epoxy resin or a novolak cresol mold epoxy resin according to the resin frame used, as for the sum total content of an above-mentioned sulfonium radical, propargyl radical and carbon-carbon double bond, it is more desirable that they are 400 or less mmol.

[0024] The resin constituent contained in the cation electrodeposition paint constituent of this invention To, for example, the epoxy resin which has at least two epoxy groups in a monod the compound (A) which has an epoxy group, the functional group which reacts, and a propargyl radical is made to react the process (i) which obtains an epoxy resin constituent with a propargyl radical — and A sulfide / acid mixture can be made to be able to react to the residual epoxy group in an epoxy resin constituents with the propargyl radical obtained at the process (i), it can manufacture suitably according to the process (ii) which introduces a sulfonium radical.

[0025] When necessary is just to use together the compound (B) which has an epoxy group, the functional group which reacts, and a carbon-carbon double bond with the above-mentioned compound (A) in the above-mentioned process (i), in piping a carbon-carbon double bond to the resin constituent contained in the cation electrodeposition paint constituent of this invention if needed.

[0026] When acetylide-izing a part of propargyl radical which the resin constituent contained in the cation electrodeposition paint constituent of this invention has, metallic compounds, such as a complex of transition metals, such as copper, silver, or bismuth, or a salt, can be made to be able to react to an epoxy resin constituent with the acetylide-ized some propargyl radicals in the above-mentioned epoxy resin constituent can be given. The resin constituent contained in the cation electrodeposition paint constituents of above-mentioned this invention can be obtained according to the manufacture approach of a publication to JP,2000-18891,A etc.

[0027] In the cation electrodeposition paint constituents of this invention, since the resin constituents which has a sulfonium radical and a propargyl radical as mentioned above is contained and the above-mentioned resin constituent has hardenability, use of a curing agent is necessarily unnecessary. However, you may use it in order to raise hardenability further. As such a curing agent, the compound which was made to carry out the addition reaction of the compound which has carbon-carbon double bonds which have propargyl radicals, such as

propargyl alcohol, such as a compound and an acrylic acid, and obtained it can be mentioned to poly epoxide, such as the compound which has two or more at least one carb in a propargyl radical and carbon-carbon double bond, for example, a novolak phenol etc. pen TAERI etc tetraacyclic ether, etc, for example.

[0028] It is not necessary to necessarily use a curing catalyst for the cation electrodeposition paint constituents of this invention. However, when it is necessary to raise hardenability further by the hardening reaction condition, the transition-metals compound usually used may be added suitably if needed. That it was not limited especially by such a compound, for example, carboxylic acids, such as formic, such as a cyclohexane and an acrylate, and an acidic acid, etc combined to transition metals, such as nickel, cobalt, manganese, palladium, and a rhodium, can be mentioned. As for the loadings of the above-mentioned curing catalyst, it is desirable that it is 0.1~2.5% of the weight to the resin solid content, weight in the above-mentioned cation electrodeposition paint constituent.

[0029] An amine can be blended with the cation electrodeposition paint constituent of this invention. By combination of the above-mentioned amine, the conversion rate to the sulfide of the sulfonium radical by the electrolytic reduction in a electrodeposited process increases. It is not limited especially by the above-mentioned amine, for example, amine compounds, such as fatty amines or monofunctional [of the class / 1st / – the 3rd class] and many organic functions, an alkylene group amine, and aromatic amine, can be mentioned. Among those, a water-soluble or water-dispersible thing is desirable, for example, can mention the alkylenimine monochloramine of the carbon numbers 2~8, such as monoethylamine, dimethylamine, a trimethylamine, triethylamine, propylamine, diisopropylamine, and triethylamine, a dimethyl amine, a methylbenzyl amine, dimethylbenzylamine, cyclohexylamine, a morpholine, N-methyl morpholine, a pyridine, pyrazine, a piperidine, imidazoline, an imidazole, etc. These may be used independently and may use two or more sorts together. Since moisture powder stability is excellent especially, hydroxy amines, such as monoethanolamine, diethanolamine, and diethylbutoxylamine, are desirable.

[0030] The above-mentioned amine can be directly blended into the cation electrodeposition paint constituent of this invention. Although the neutralization acid in resin will be taken and the stability of an electrodeposited solution will get worse remarkably in the cation electrodeposition paint of the conventional neutralizer acid amine system if the amine of isolation is added, inhibition of such bath stability does not arise in this invention.

[0031] The loadings of the above-mentioned amine have per 100g of resin solid content in the cation electrodeposition paint constituents of this invention, and desirable 0.3~5mmol, if sufficient effectiveness cannot be secured to throwing power of electrolyte colouring so they are 0.3~5mmol (i) / less than 100g, but it exceeds 25mmol / 100g, effectiveness according to an addition amount is required. It is unconventional. They are 1~5mmol / 100g more preferably.

[0032] The cation electrodeposition paint constituent of this invention may contain further the other components used for the usual cation electrodeposition paint if needed. It is not limited especially as the above and other components, for example, additives for coatings, such as a pigment, a rust-proofer, pigment-content powder resin, a surfactant, an antioxidant, and an ultraviolet ray absorber, etc, can be mentioned.

[0033] It is not limited especially as the above-mentioned pigment, for example, is used for a cation electrodeposition paint generally [extenders, such as rust preventive pigment; kaolins, such as color pigments basicic silicic acid lead, such as a titanium dioxide, carbon black, and red ochre, and molybdatephosphate acid aluminum, clay, and talc, etc.] can be mentioned. Specifically as the above-mentioned rust-proofer, phosphorous acid calcium, phosphorous acid zinc, calcium, a calcium support silica, a calcium support zeolite, etc, can be mentioned. As for the sum total loadings of the above-mentioned pigment and a rust-proofer, it is desirable that it is 0~50% of the weight as solid content in the cation electrodeposition paint constituent of this invention.

[0034] The above-mentioned pigment-content powder resin is used in order to stabilize and distribute the above-mentioned pigment in a cation electrodeposition paint. Especially as pigment-content powder resin, it is not limited and the pigment-content powder resin currently generally used can be used. Moreover, the pigment-content powder resin containing a sulfonium

radical] and an unsaturated bond may be used into resin. The pigment-content powder resin containing such a sulfonium radical and an unsaturated bond can be obtained by the approach of making a sulfide compound reacting to the hydrophilic epoxy resin which for example, a bisphenol mold epoxy resin and half blockized isocyanate are made reaction, and it is obtained, or making a sulfide compound reacting to the above-mentioned resin under existence of a monohydric acid and a hydroxy-group content dibasic acid etc. The above-mentioned pigment-content powder resin can be made to also stabilize and distribute the above-mentioned non-heme metal rust-proofer in a cation electrodeposition paint.

[0035] To the above-mentioned resin constituent contained in this, if needed, the cation electrodeposition paint constituent of this invention can mix each above-mentioned component, and can obtain it by dissolving or distributing in water etc. An above-mentioned photopolymerization initiator may be blended by preceding preparing the above-mentioned cation electrodeposition paint constituent, and distributing the above-mentioned resin constituent, and after pasting in addition to above-mentioned pigment-content powder resin, it may be blended by adding the paste obtained after the time of manufacture of the above-mentioned casting constituent, or manufacture. As for the above-mentioned cation electrodeposition paint constituent, it is desirable to adjust so that it may not deviate from the range of above-mentioned [the content of the propargyl radical in the resin constituent contained in it's = carbon-carbon double bond, and a sulfonium radical]. In case it uses for cation electrodeposition, as for the above-mentioned cation electrodeposition paint constituent, it is desirable to be prepared so that a novolak resin may serve as 10~30% of both liquid.

[0036] The paint film formation approach of the above-mentioned cation electrodeposition paint constituent to a coated object, and includes the process which performs an optical exposure in the coat obtained. The paint film formation approach of this invention may include the process which heats further the coat obtained by electrocoating. If it does not deteriorate by not being limited and carrying out cation electrodeposition especially as a coated object used for the paint film formation approach of this invention, when it will not be limited but will heat especially, it is still more desirable that it is what does not characterize with heating. As such a coated object, what carried out surface treatment of plates, such as a grid, a cast plate, and aluminum, molding, and them can be mentioned, for example.

[0037] The above-mentioned electroprinting uses a coated object as cathode, between anodes plate, impresses the electrical potential difference of 50~50V, and usually performs it. If it becomes being less than 10~15V, electrodepositing applied voltage inadequate and it exceeds 450V, power consumption becomes large and is uneconomical. A uniform coat can be formed in the whole coated object without producing the rapid rise of thickness in an electrodeposited process, if it is within the limit and an electrical potential difference is impressed [above-mentioned] using an above-mentioned cation electrodeposition paint constituent. The bath liquid temperature of the above-mentioned cation electrodeposition paint constituent in the case of increasing the above-mentioned electrical potential differences usually has desirable 10~45 degrees C.

[0038] the process to which the electric resistances value per unit volume of the above-mentioned coat is made to increase by the above-mentioned electroprinting's using an anode the process and the above-mentioned coated object which are immersed in the above-mentioned cation electrodeposition paint constituent in a coated object, impressing an electrical potential difference between anode plates, and increasing an electrical potential difference to the process in which a coat is deposited and the deposited above-mentioned coat, further — since — being constituted is desirable. Although the above-mentioned electrical-potential-difference impressing time amounts changes with electrodeposited conditions, generally it can be made into 2~4 minutes. Thus, after termination of an electrodeposited process, cation electrodeposition the non-hardened coat obtained is set remaining as it is or after rinsing.

[0039] Subsequently the above-mentioned coat non-hardened [electrodeposited] starts a polymerization by optical exposure, and is hardened. As the above-mentioned optical exposure, the point of hardenability and versatility to UV irradiation is desirable. Although hardening

processes so that there are generally many exposures, 200~3000 mJ·cm⁻² is desirable. If hardening may become less than 200 mJ·cm⁻² inadequate and 5000 mJ·cm⁻² is exceeded, whenever [hardening] may not increase considering on exposure but it may become uneconomical. It is 900~3000 mJ·cm⁻² more preferably.

[0040] Generally the above-mentioned exposure is expressed by the degree type.

[Exposure (mJ·cm⁻²) = [exposure on the strength (mJ·cm⁻²·s⁻¹)] × irradiation time (s)]

The reverse, the case where we determine the above-mentioned exposure by choosing exposure reinforcement and irradiation time respectively, for example, it irradiates for 0.2~20 minutes by the exposure reinforcement 30~1200 mJ·cm⁻² is mentioned.

[0041] It is not limited especially as the approach of the above-mentioned optical exposure, for example, a well-known approach can be used conventionally. When the above-mentioned optical exposure is UV irradiation, a high pressure mercury vapor lamp, a chemical lamp, etc can be chosen suitably, corresponding to hardening conditions, such as exposure reinforcement and irradiation time. For example, since exposure reinforcement is 1.0~20 mJ·cm⁻²·s⁻¹, as for irradiation time, for 1~30 minutes is usually desirable [since peak wavelength is 200~400nm and exposure reinforcement is usually 200~1000 mJ·cm⁻²·s⁻¹ when using a high pressure mercury vapor lamp as for irradiation time for 0.2~10 minutes is desirable, and], when using a chemical lamp.

[0042] Not only the above-mentioned optical exposure but the process to heat may be given to the coat obtained by the above-mentioned steel-hardening non-hardened [electrodeposited]. As heating conditions, the obtained coated object is thrown into the drying furnace set as 120~240 degrees C, and heating for 5~60 minutes is mentioned to it, for example. In this invention, since the photo-polymerization inhibitor contains in the cation electrodeposition paint constituent and hardening, by photopolymerization is performed, it is sufficient to be able to make it harden in low temperature and a short time rather than the heat hardening of the conventional electrodeposited coat, for example, to heat for 10~45 minutes at 150~210 degrees C preferably, and it is sufficient to heat for 10~30 minutes at 130~180 degrees C more preferably.

[0043] When heating a coat in the paint film formation approach of this invention, as for whenever [above-mentioned steaming temperature], it is desirable to set it as temperature higher 1~15 degrees C than the curing temperature of an above-mentioned cation electrodeposition paint constituent, and as for the curing temperature of the above-mentioned cation electrodeposition paint constituent, it is desirable to be set as 130~220 degrees C. When surface temperature is low temperature from 130 degrees C, there is a possibility that the smooth nature of the paint film obtained may fall. There is a possibility that the appearance of the multi-layer paint film obtained when the physical properties of the paint film obtained full when curing temperature is an elevated temperature from 220 degrees C, or painting top coat etc, it may fall. A setup of the above-mentioned curing temperature can be given to this controller called adjustment of the class of a hardening functional group, a curing agent and catalyst, an amine, etc, by the well-known approach.

[0044] The curing temperature in this invention means the temperature for obtaining the paint film of 85% of gel molar fractions with heating for 25 minutes. Measurement of the above-mentioned gel molar fraction is performed by the approach of computing from the weight difference of the test color card before and behind a trial at the time of being immersed in oil, and making a test color card flow back for 5 hours.

[0045] When heating the above-mentioned coat non-hardened [electrodeposited] in the paint film formation approach of this invention, the above-mentioned heating is separately [as the optical exposure of the above-mentioned coat non-hardened / electrodeposited] good in line. In this case, since an above-mentioned photopolymerization inhibitor is used in this invention, in order to operate this effectively, after performing the above-mentioned optical exposure, it is desirable to perform the above-mentioned heating.

[0046] As for the paint film formation approach of this invention, it is desirable to include the process which performs the above-mentioned heating and the above-mentioned optical exposure to coincidence to the above-mentioned coat non-hardened [electrodeposited]. When the process which performs the above-mentioned heating and the above-mentioned optical

exposure to coincidence is included in all or a part of time amount which performs the above-mentioned optical exposure, the above-mentioned heating can be performed to coincidence. For example, although the process which performs only the above-mentioned heating other than the process which performs the above-mentioned heating and the above-mentioned optical exposure to coincidence, and/or the process which performs only the above-mentioned optical exposure to coincidence, and/or the process which performs the above-mentioned optical exposure are included, it is desirable to perform the above-mentioned heating to coincidence from the point of hardenability in all of time amount that perform the above-mentioned optical exposure. Adjustment of the time amount which performs the above-mentioned optical exposure can be performed by, for example, adjusting the reinforcement of an optical exposure suitably as mentioned above.

[0051] In the cation electropainting approach of this invention, on the electrodeposited coat obtained by cation electrodepositing, if needed, in order to give substrate concealment nature and chipper-proof nature, an intermediate coat may be applied, and two coats of top coat may be further given for exploring the improvement in appearance, etc. It is desirable to make κ harder after applying of an intermediate coat, since hardening according [on this invention and / the above-mentioned electrodeposited coat] to an optical exposure at least is made to perform.

[0052] Since the carbon electrodeposition paint constituent of this invention contains a resin constituent with a sulfonium radical and a propagyl radical, the electrodeposited paint film excellent in throwing power of electrolytic colouring is obtained. Coat hardening by photopolymerization which did not have the carbon electrodeposition paint constituent of this invention in conventional automobile car body and electrodeposition paint for composites since the radical occurred by the sulfonium radical, it acted on the partial saturation double bond in which the above-mentioned radical is contained by a propagyl radical and the case and the polymerization reaction advanced when the optical exposure was performed to the non-hardened electrodeposition coat obtained by electropainting, since an above-mentioned photopolymerization initiator is included again to realize. Thereby, compared with the conventional heat hardening, hardening in low temperature and a short time is attained, and advantageous effectiveness, such as expansion of the selection width of face of the electropainting and the hardening conditions of being able to adopt a photopolymerization hardening system besides the weatherproof improvement not only in the cost reduction by energy saving and short-time-heating but the hardening coat obtained, a low thermal-resistance base material, and cold cure, is acquired. By performing optical exposure and heating to coincidence, the above-mentioned hardening can improve further and can attain further low-temperature-heating and short-time-heating of hardening. Therefore, the coated object which has the coat obtained by the paint film formation approach and the above-mentioned paint film formation approach using the cation electrodeposition paint constituent of this invention and the above-mentioned cation electrodeposition paint constituent is used especially suitable for electropainting, such as a car body of an automobile, and components.

[0053]

[Example] Although an example is hung up over below and this invention is explained to it in more detail, this invention is not limited only to these examples. Example 1 of manufacture In addition to the flask equipped with an agitator, a thermometer, nitrogen installation tube, and a reflux cooling pipe, carried out the temperature up of anisole 30.0g, and the dimethyl benzylamine 0.2g to 125 degrees C. It was made to react to 100.0g (EPO TOTO YDON-701, Tofuku Kasei Co., Ltd. make) of o-cresol novolak mold epoxy resins of the manufacture weight per epoxy equivalent 200.4 of an epoxy resin constituent with a sulfonium radical and a propagyl radical for 3 hours, and the resin which has the propagyl radical of weight per epoxy equivalent 1600 was obtained. Furthermore, 109.0g of this reaction was divided to the flask equipped with an agitator, a thermometer, nitrogen installation tube, and a reflux cooling pipe, 1-(2-hydroxyethyl)tri-2 and 3-propenamide 0.9g, 3.3g of glass bead media, and 6.4g of deionized water were put in, the temperature up was carried out to 75 degrees C, and it was made to react for 6 hours. It checked that the residual acid number was smaller than 5. 28.0g of deionized water was added further, and the target resin solution was obtained.

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the cold cure of it may become possible, and heating may be used together, by performing heating to an optical exposure and coincidence, hardenability improves and cold cure and short-time hardening are promoted further. Therefore, the coated object which has the coat obtained by the cation electrodeposition paint constituents, the paint film formation approach, and the above-mentioned approach of this invention is used suitable for paint of the car body of an automobile, or components.

[Translation done.]

Solid content concentration was 70.0 % of the weight, and number average molecular weight was 2100. [0054] The water paint liquid whose solid content concentration is once 50% was prepared having added deionized water to the resin solution obtained in the example 1 of example 1 (manufacture of carbon electrodeposition paint constituent) manufacture gradually, and fully stirring by DISIPPA. To this, 3 % of the weight and pure water were added for benzyl dimethyl ketal (URUGAKYUJA IRB631, Chiba Gelgy make) to raise solid content weight as a photopolymerization initiator, and the carbon electrodeposition paint constituent whose solid content concentration is 15% was obtained. When the curing temperature of this carbon electrodeposition paint constituent was measured, it was 180 degrees C.

[0055] (The cation electropainting approach) The obtained cation electrodeposition paint constituent was moved to the stainless steel container, and it considered as the electrodeposited bath, and electropainting was performed so that it might become 10 micrometers of decoration thickness as a coated object here, at the cold rolled steel plate (phosphoric-acid zinc processing agent surfboard dry by Nippon Paint Co., Ltd. JIS G3141 SPCO-SD, SD= 5000 processing) which carried out phosphoric-acid zinc processing served as cathode. With the condition of having raised the coated object pulled up from the electrodeposited bath after electropainting and in a stainless steel container on the oil level, it rinsed after making it acetone naturally for 30 seconds, and it is a high pressure mercury vapor lamp (the peak wavelength of 365nm). After performing UV irradiation for 1 minutes using exposure of the strength 500 mJ·cm⁻²·s⁻¹ and the OAK CO., LTD. make, the color card was created by heating for 25 minutes on which 150 degrees C, 160 degrees C, 170 degrees C, 180 degrees C, and 200 degrees C temperature.

[0056] (Evaluation of hardenability) The paint plate which carried out in this way and was created was put into the Soxhlet extactor, it extracted under the reflux condition for 6 hours using the mixed liquor of an acetone / methanol = 1/1, and the gel molar fraction of the hardening paint film was computed according to the degree type, a gel molar fraction = (%) = extract Shigaku Ushiro (g) / extract Sakai (Shigaku) (g) × 100 result was shown in Table 1.

[0057] Performing example 2 UV irradiation for 25 minutes using the chemical lamp (IE-A2, exposure reinforcement of 5.5mW, the JEOL energy machine company make), everything but heating for 25 minutes to this and coincidence created and evaluated the color card like the example 1. In addition, the amount of UV irradiation is the same as an example 1. A result is shown in Table 1.

Everything but heating for 25 minutes created and evaluated the color card like the example 1, without performing example UV irradiation of reference. A result is shown in Table 1.

[Table 1]

EXPERIMENT	EXPERIMENTAL CONDITIONS (%)					
	150°C	160°C	170°C	180°C	190°C	200°C
example 1 (reference)	65	65	50	44	39	39
example 1 (present)	97	99	99	95	92	92
example 2 (reference)	89	83	65	50	40	32

[0058] Although it was inferior to hardenability from Table 1 in the example of reference which does not perform UV irradiation since the gel molar fraction was low, in the example 1 which performs UV irradiation apart from heating, hardenability improved and it turned out that hardenability is further excellent in the example 2 which performs UV irradiation to heating and coincidence.

[0059]

(Effect of the invention) Since the carbon electrodeposition paint constituent of this invention contains of an above-mentioned configuration, photopolymerization can be made to perform paint film hardening after cation electropainting, and cold cure and short-time hardening are realized. Since the paint film formation approach of this invention performs an optical exposure.

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